

Chemistry

Lecture 16

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Thermochemistry and energetics of chemical reactions

Outline:

- ✚ System, Surrounding and State function
- ✚ Definitions of terms used in thermodynamics
- ✚ Standard states and standard enthalpy changes
- ✚ Energy in chemical reaction (thermal energy)
- ✚ 1st law of thermodynamics
- ✚ Sign of ΔH
- ✚ Enthalpy of reaction
- ✚ Hess's law to construct simple energy cycles

Thermodynamics

"The study of all types of energy changes associated with physical and chemical changes"

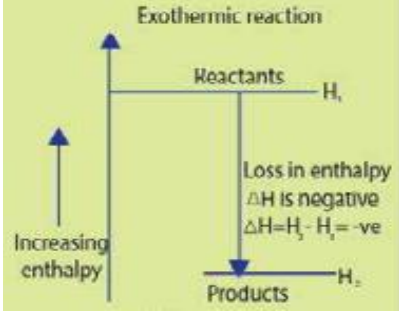
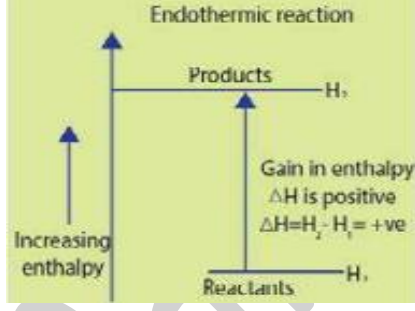
Thermochemistry

- ❖ Based on 1st law of thermodynamics
- ❖ Study of heat changes during chemical reaction

Thermo-chemical Equation:

- ❖ Gives the values of heat changes during reaction (measured in terms of the enthalpy changes ΔH)
- ❖ The equation that gives physical states of reactants and products
- ❖ When a chemical equation is reversed, the magnitude of the ΔH remains same but its sign is reversed
- ❖ The coefficients of various substances of chemical equation represents the number of their respective moles
- ❖ If coefficients in the chemical equation are multiplied or divided by some number, the ΔH value must also be multiplied or divided by the same number

Exothermic Reactions	Endothermic Reactions
Heat evolved by system	Heat absorbed by system
$\Delta H = \text{negative}$	$\Delta H = \text{positive}$
Temperature of system first rises, then becomes equal to room temperature Extra heat travels to surrounding thereby increasing 'T' of surrounding	Temperature of system first decreases, then becomes equal to room temperature Heat travels from surrounding to system, so 'T' of surrounding decreases

Heat travels from system to surrounding	Heat travels from surrounding to system
No. of bond formed is greater than bond breakage	No. of bond formed is lesser than bond breakage
Most spontaneous reactions are exothermic	Most non-spontaneous reactions are endothermic
Enthalpy content of reactant is higher than product i.e. $H_R > H_P$	Enthalpy content of reactant is lower than product i.e. $H_R < H_P$
Products are more stable than reactants	Reactants are more stable than products
	
$C(s) + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H = -393.7 \text{ kJmol}^{-1}$	$N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)} \quad \Delta H = +180.5 \text{ kJmol}^{-1}$
Process of Respiration	Photosynthesis and Evaporation

System:

- Anything under consideration/experimentation
- **Open system** (Both mass & heat can flow across)
- **Closed system** (Only heat can flow across)
- **Isolated system** (Both mass & heat cannot flow across)

Surrounding:

- Everything except the system
- ☞ Equilibrium b/w system and surrounding gives reversible reactions

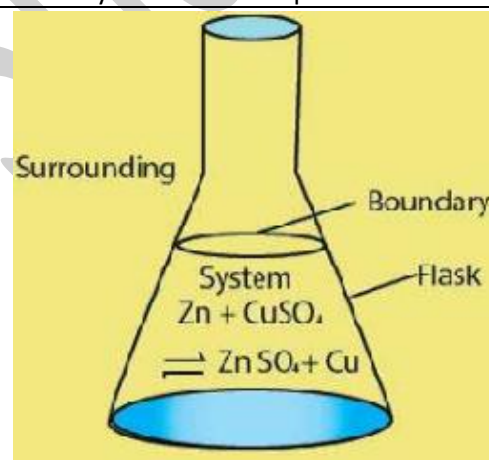
Boundary:

- Imaginary line separating system from surrounding

State Function:

- Macroscopic property of system
- Has initial and final states
- Independent of path followed to bring the change
- **Examples:** Pressure, Temperature, Volume, Internal energy (E), Enthalpy (H), Entropy (S), Gibbs free energy (G) [$\Delta G > 0$ (non-spontaneous process), $\Delta G < 0$ (spontaneous process), $\Delta G = 0$ (process at equilibrium)]
- Their absolute values aren't measured but change is measured ($\Delta E = E_2 - E_1$)

Internal Energy:



- Sum of all possible energies of the system $E = K.E + P.E$
- K.E is due to translational, vibrational and rotational motions of particles
- P.E is due to all types of attractive forces present in the system
- Units: J, calorie
- **Joule:** Energy required to move an object or a particle through a distance of 1 meter by a force of 1 Newton
- **Calorie:** Heat or thermal energy required to raise the temperature of one gram of water from 14.5 to 15.5°C. $1 \text{ calorie} = 4.18 \text{ J}$

Heat Capacity:

- The amount of heat required to raise the temperature of given amount of a substance by 1 Kelvin
- Expressed in JK^{-1}
 - **Specific heat capacity:** The amount of heat required to raise the temperature of one gram of substance by 1 Kelvin
 - Expressed in $\text{Jg}^{-1}\text{K}^{-1}$
 - **Molar heat capacity:** The amount of heat required to raise the temperature of one mole of a substance by 1 Kelvin
 - $\text{JK}^{-1}\text{mole}^{-1}$

Modes of Transference of Energy:

Heat (q)	Work (w)
Energy that flows across the boundary of a system during a change in its state due to the difference in temperature between the system and the surroundings. (random form of energy)	It is defined as the product of force and distance. In thermo-chemistry, we study pressure-volume work
It occurs when there is difference in temperature b/w system and surrounding	Occurs if system involves gaseous substances and there is pressure difference b/w system and surrounding
Not a state function so path dependent (so $q = q_1 + q_2 + q_3 + \dots$)	Not a state function so path dependent (so $w = w_1 + w_2 + w_3 + \dots$)
Units; J, kJ, Calories	Units; J, ergs (CGS system)
q = +ve (Heat absorbed by system) q = -ve (Heat evolved by system)	w = +ve (Work done on system) w = -ve (Work done by system)
(q + w) is a state function	

1st Law of Thermodynamics

- ☞ Also called the law of conservation of energy
- ☞ States that energy can neither be created nor destroyed, but can be changed from one form to another
- ☞ Internal energy (sum of all possible energies i.e. K.E + P.E) change is given as;

$$\Delta E = q + w$$

$$\Delta E = q - P\Delta V \quad (\text{work done by system to move piston upwards, so } w = -P\Delta V)$$

$$\Delta E = q_v - P(0) \quad (\Delta V = 0, \text{ as volume is constant})$$

$$\Delta E = q_v$$

☞ This shows that a change in internal energy of a system, at constant volume is equal to heat absorbed by the system (q_v)

☞ Enthalpy (H):

☞ Total heat content of system

☞ Enthalpy is equal to the internal energy, E plus the product of pressure and volume (PV)

$$H = E + PV$$

$$\Delta H = \Delta E + \Delta(PV)$$

$$\Delta H = \Delta E + P\Delta V + V\Delta P$$

$$\Delta H = \Delta E + P\Delta V + V(0) \quad (\Delta P = 0, \text{ as } P \text{ is constant})$$

$$\Delta H = \Delta E + P\Delta V \text{ (For Gases)} \rightarrow (i) \quad [\Delta H \approx \Delta E \text{ for liquids/solids as no } V \text{ changes}]$$

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q_p$$

☞ This shows that change in enthalpy is equal to heat of reaction at constant pressure

$$\blacklozenge q_p > q_v$$

Energy Change of Reaction

Standard conditions:

◆ 1 mole, 25°C (298 K), 1 atm

Important Terms:

◆ $\Delta H = H_P - H_R$

◆ ΔH^0 = standard enthalpy change

◆ ΔE = internal energy change

◆ ΔS = entropy change

◆ ΔG = free energy change

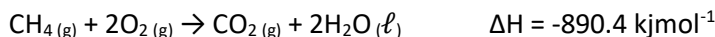
Enthalpy of Reaction (ΔH^0_r):

☞ Depends upon;

- i. Physical states of reactants and products
- ii. Temperature during reaction
- iii. Pressure during reaction
- iv. Quantities (moles) of reactant/product
- v. Nature of the reactants

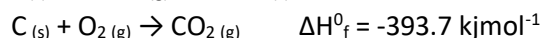
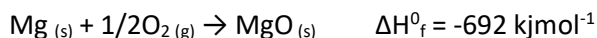
☞ Amount of heat evolved or absorbed when certain number of moles of reactant react completely to give product under standard conditions





Enthalpy of Formation (ΔH_f°):

- For compounds
- Amount of heat evolved or absorbed when 1 mole of compound is formed from its elements under standard conditions



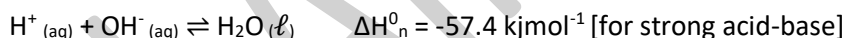
Enthalpy of Atomization ($\Delta H_{\text{at}}^\circ$):

- For elements
- Amount of heat absorbed when 1 mole of gaseous atom is formed from its element under standard conditions



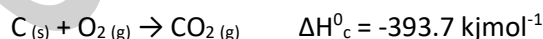
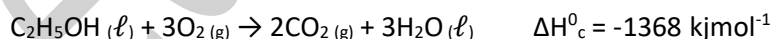
Enthalpy of Neutralization (ΔH_n°):

- For acid-base reactions
- Amount of heat evolved when 1 mole of H^+ (from acid) reacts with 1 mole of OH^- (from base) to form 1 mole of water under standard conditions



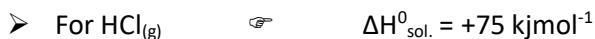
Enthalpy of Combustion (ΔH_c°):

- For substances (either element or compound)
- Amount of heat evolved when 1 mole of substance is burnt completely in excess of oxygen under standard conditions



Enthalpy of Solution ($\Delta H_{\text{sol.}}^\circ$):

- For solutions
- Amount of heat evolved or absorbed when 1 mole of substance is dissolved in so much solvent that further dilution results no detectable heat change under standard conditions



Measurement of ΔH° :

Experimentally by calorimeters		Calculated by Hess's Law
Glass Calorimeter	Bomb Calorimeter	Applicable for;

ΔH^0_n is measured	ΔH^0_c is measured	<div>i. One step reaction</div> <div>ii. For multi step reactions (specially) $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$</div> <div>Born-Haber cycle is application of Hess's law used for ionic compounds</div>
$\Delta H^0_n = q = m \times s \times \Delta T$	$\Delta H^0_c = q = c \times \Delta T$	
<div>q = heat evolved m = mass of substance S = specific heat($\text{JK}^{-1}\text{g}^{-1}$) ΔT = 'T' change</div>	c = heat capacity	
Calorimeters only applicable for 1 step reactions		

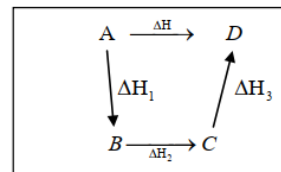
Hess's Law (Q.16, Q.17, Q.18, Q.19, Q.20)

- ◆ If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same

According to Hess's law, $\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$

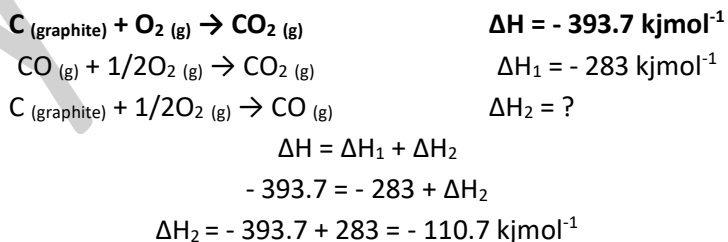
Mathematically, $\sum \Delta H(\text{cycle}) = 0$

Of course, Hess's law is simply an application of the more fundamental law of conservation of energy. So, $\sum \Delta H(\text{cycle}) = 0$



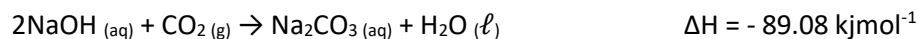
- ◆ ΔH for many compounds cannot be measured directly from calorimeter like;
 - CCl_4 cannot be prepared directly by combining carbon and chlorine. Similarly, it does not decompose easily into its constituent elements.
 - Boron oxide (B_2O_3) and aluminium oxide (Al_2O_3) form protective layer of oxides covers the surface of the unreacted element.
 - Formation of CO cannot be measured directly due to the formation of CO_2 with it.

Enthalpy of formation of CO:



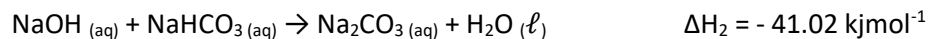
Formation of Sodium carbonate: verification of Hess's law

Single step process:



Two step process:





$$\begin{aligned}\Delta H &= \Delta H_1 + \Delta H_2 \\ -89.08 &= -48.06 + (-41.02) \\ -89.08 &= -89.08\end{aligned}$$

Applications:

- Heat of combustion
- Heat of formation
- Indirect enthalpy change measurements
- Lattice energy (Born-Haber cycle)

Q.16: By applying Hess's law, calculate the enthalpy change for the formation of an aqueous solution of NH_4Cl from NH_3 gas and HCl gas. The results for the various reactions are as follows;

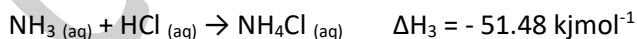


Solution:

Path 1 (Direct route as asked in question)



Path 2 (Indirect route as given in question)



$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$$

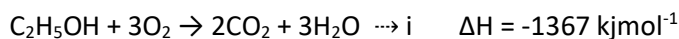
$$\Delta H = (-35.16) + (-72.41) + (-51.48) = -159.05 \text{ kJmol}^{-1}$$

Q.17: Calculate the heat of formation of ethyl alcohol from the following information;

- i. Heat of combustion of ethyl alcohol is -1367 kJmol^{-1}
- ii. Heat of formation of carbon dioxide is $-393.7 \text{ kJmol}^{-1}$
- iii. Heat of formation of water is $-285.8 \text{ kJmol}^{-1}$

Solution:

Heat of combustion of ethyl alcohol is -1367 kJmol^{-1}



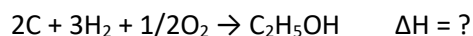
Heat of formation of carbon dioxide is $-393.7 \text{ kJmol}^{-1}$



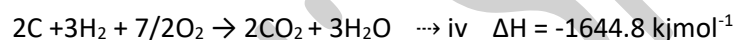
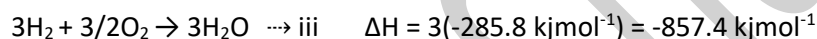
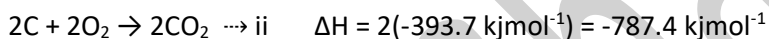
Heat of formation of water is $-285.8 \text{ kJmol}^{-1}$



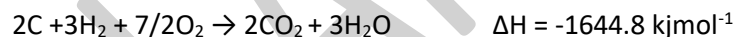
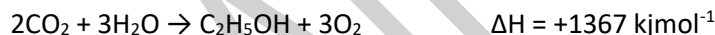
Requirement is heat of formation of ethyl alcohol;



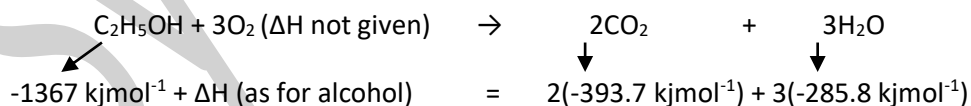
Multiply eq. (ii) with 2, eq. (iii) with 3 and then add them



Invert eq. (i) [when eq. is inverted sign of ΔH changes] and add it to eq. (iv)



SHORT CUT



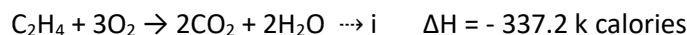
$$\Delta H = -787.4 \text{ kJmol}^{-1} + (-857.4 \text{ kJmol}^{-1}) + 1367 \text{ kJmol}^{-1}$$

$$\Delta H = -277.8 \text{ kJmol}^{-1}$$

Q.18: If the heats of combustion of C_2H_4 , H_2 and C_2H_6 are -337.2 , -68.3 and -372.8 k calories respectively, then calculate the heat of the following reaction; $\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$

Solution:

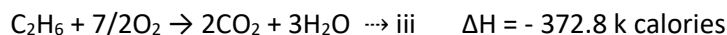
Heat of combustion of C_2H_4 ;



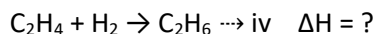
Heat of combustion of H_2 ;



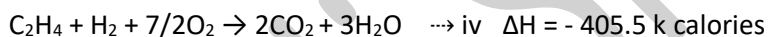
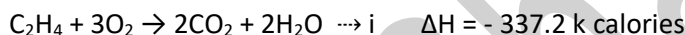
Heat of combustion of C_2H_6 ;



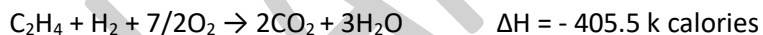
Requirement is heat of formation of C_2H_6 ;



Add eq. (i) and eq. (ii)



Invert eq. (iii) [when eq. is inverted sign of ΔH changes] and add it to eq. (iv)



SHORT CUT



$$\Delta H = -337.2 \text{ k calories} - 68.3 \text{ k calories} + 372.8 \text{ k calories}$$

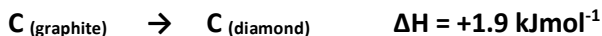
$$\Delta H = -32.7 \text{ k calories}$$

Q.19: Graphite and diamond are two forms of carbon. The enthalpy of combustion of graphite at 25°C is $-393.51 \text{ kJmol}^{-1}$ and that of diamond is $-395.41 \text{ kJmol}^{-1}$. What is the enthalpy change of the process Graphite \rightarrow Diamond at the same temperature?

Solution:

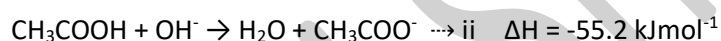
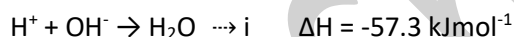


For Graphite \rightarrow Diamond, invert eq. (ii) and add with eq. (i)

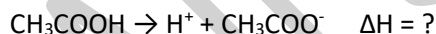


Q.20: If the heat of neutralization of HCl and NaOH is -57.3 kJmol^{-1} and heat of neutralization of CH_3COOH with NaOH is -55.2 kJmol^{-1} , calculate the enthalpy of ionization of CH_3COOH .

Solution:



Required:



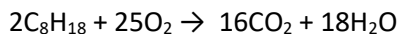
Invert eq. (i) and add with eq. (ii)



Enthalpies of Reactions from enthalpy of formation

Enthalpy of solution = (sum of enthalpies of products) – (sum of enthalpies of reactant)

Q. Calculate ΔH of reaction for the following reaction, which take place when gasoline burns in internal combustion engines. Where the values of ΔH_f^0 are -269 kJ , 0 kJ , -393.5 kJ and -285 kJ for C_8H_{18} , O_2 , CO_2 and H_2O respectively



$$\Delta H_{\text{reaction}}^0 = [16 (-393.5) + 18 (-285.8)] - [2 (-269) + 25 (0)]$$

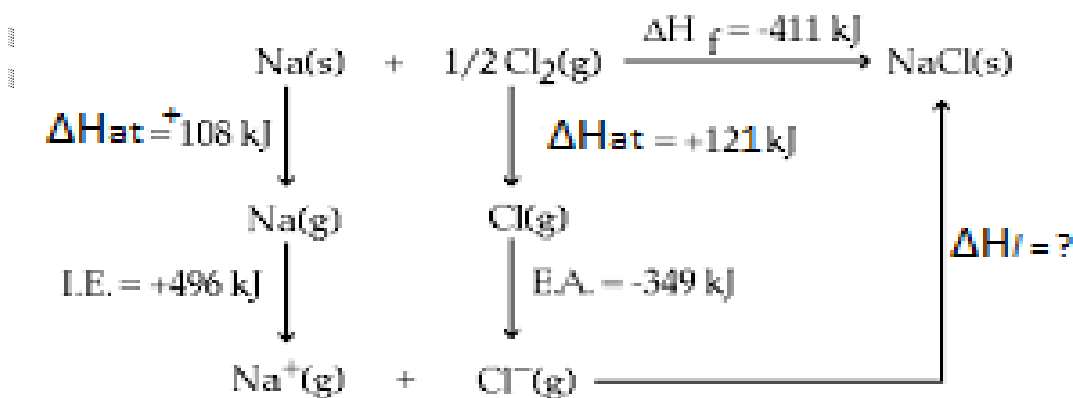
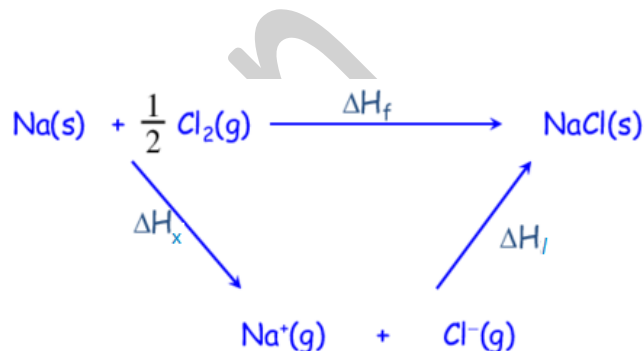
$$\Delta H_{\text{reaction}}^0 = -10902.4 \text{ kJ} = -1.09 \times 10^4 \text{ kJ}$$

Born Haber Cycle (As precaution)

- Used to calculate lattice energy
- Lattice Energy:** Energy released when 1 mole of ionic compound is formed from its gaseous ions
OR energy required to break 1 mole of ionic compound into its gaseous ions
- $L.E \propto \text{charge}$, $L.E \propto 1/\text{size}$, $L.E \propto \text{packing of ions}$ [$\text{NaF} > \text{NaCl} > \text{NaBr} > \text{NaI}$]
- Information from L.E:**
 - Structure of ionic solids
 - Properties of ionic solids
 - Strength of bonding

L.E of NaCl [Q.21 (c) on similar lines]

- Applying Hess's law
- $\Delta H_f = \Delta H_x + \Delta H_l$
- $\Delta H_l = \Delta H_f - \Delta H_x$
- To find ΔH_x represents multiple enthalpy changes, so Born Haber cycle is used for the calculation



$$\Delta H_x = \Delta H_{\text{at(Na)}} + \Delta H_{\text{I.E}} + \Delta H_{\text{at(Cl)}} + \Delta H_{\text{E.A}}$$

$$\Delta H_x = +108 + 496 + 121 - 349$$

$$\Delta H_x = +376 \text{ kJmol}^{-1}$$

➤ As $\Delta H_l = \Delta H_f - \Delta H_x$

$$\Delta H_l = -411 - (+376)$$

$$\Delta H_l = -787 \text{ kJmol}^{-1}$$